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An Improved Method for Determining the
Equivalent Conductances of Strong
Electrolytes at Infinite Dilution

Chemistry

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AN IMPROVED METHOD FOR DETERMINING THE
EQUIVALENT CONDUCTANCES OF STRONG
ELECTROLYTES AT INFINITE DILUTION

BY

JAMES EDGAR BELL
S. B. University of Chicago,
1905.

THESIS

Submitted in Partial Fulfillment of the Requirements for the

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May 12, 1913.

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

James Edgar Bell

ENTITLED AN IMPROVED METHOD FOR DETERMINING THE EQUIVALENT CONDUCTANCE
OF STRONG ELECTROLYTES AT INFINITE DILUTION.

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF

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Committee

on

Final Examination

247344



The present work was undertaken at the suggestion of Professor E. W. Washburn, and has been carried out under his direction. Professor Washburn has always been ready with fruitful suggestions and methods of attack, and my thanks are due him for his assistance and encouragement.

AN IMPROVED METHOD FOR DETERMINING THE EQUIVALENT CONDUCTANCE OF STRONG ELECTROLYTES AT INFINITE DILUTION.

PART I.

THE NATURE OF THE PROBLEM.

Introduction.

Equivalent conductances of aqueous solutions of salts are, as a rule, not determined at higher dilutions than ten-thousandth normal. A few experiments¹ have been made with solutions more dilute but the experimental errors in such work are very large and the values obtained are known to be unreliable. In fact there is considerable doubt as to the accuracy of the values commonly accepted for ten-thousandth normal solutions. This uncertainty is due to the following three sources of error.

(1) In all conductivity experiments in highly dilute solutions there is a large "water correction" necessary and the exact magnitude of this correction and the proper method of applying it is very uncertain.

(2) If solutions are made up in contact with the air, this is always a fruitful source of contamination and one which has never been taken into account.

1. Whitham and Paine, Proc. Roy. Soc., 81, 58 (1908) have measured the conductivity of .00005 N H₂SO₄, and Kohlrausch and Maltby, Abhandl. Physik. Tech. Reichanstalt, 3, 206 (1900) have made measurements on some alkali chlorides and nitrates at greater dilutions.

If they are allowed to stand in glass vessels the glass becomes a probable source of pollution.

(3) The specific resistance of solutions of such low concentrations is very large and the difficulty in making accurate measurements is thereby greatly increased.

The Water Correction.

That the conductivity of the water itself must be taken into account can readily be seen from a consideration of the measurements made by Kohlrausch and Maltby¹ on the alkali chlorides and nitrates. These experimenters made their solutions from water having a specific conductivity ranging from $.9 \times 10^{-6}$ to 1.06×10^{-8} reciprocal ohms. The accompanying table affords a comparison of the specific conductances of NaCl solutions at different concentrations, with the specific conductance of the water used in making the solutions.

Conc. of NaCl	Specific Conductance times 10 ⁶
.001 N	106.48 mhos
.0001	10.81
.00001	1.089 ²
.000001	.109 ²
Water	1.03

One can readily see that the water correction to be applied to the measured specific conductance is about 1 per cent for .001 N; 9 o/o for .0001 N; and 50 per cent for .00001 N NaCl, while the determination of the conductance of millionth normal NaCl would be little better than a rough guess. By knowing the conductivity of the water and applying the correction fairly accurate results might be obtained in solutions down to .0001 N or even .00001 N, were it not for the doubtful effect of added salts on the impurities and consequently on the initial conductance of the water. This uncertain factor in experiments of this

1. Kohlrausch and Maltby, Loc. cit.; also Sitz. ber. Königl Preuss. Akad., 1899 665.

2. In this case the calculated value at infinite dilution is used; the other values are from Kohlrausch and Maltby's data.

kind can not be entirely eliminated but can be reduced by the use of pure water, i. e. water of smaller specific conductivity. If water could be obtained whose initial specific conductance were negligible in comparison with that of the salt, as it is in higher concentrations, correct values would be obtained. It seems highly improbable, however, that solutions of this kind will be made for concentrations as low as .0001 N since a solution of this strength made from the purest water ever obtained¹ would have a water correction at 18° C of nearly .4 per cent in case of NaCl. It might not be without interest to note what the water correction would be for solutions of NaCl and KCl of different concentrations and at different temperatures if this "perfectly pure" water of Kohlrausch and Heydweiller were used in their preparation. The following table gives the corrections in per cent of total conductances of solutions of these two salts.

Concentration of salt	Water Correction					
	NaCl		KCl			
	0°	18°	25°	0°	18°	25°
.0001 N	.2	.4	.46	.17	.3	.38
.00001 N	2.0	3.5	4.4	1.7	3.0	3.7
.000001 N	17.	27.	31.+	15.	23.	28.

These figures take no account of the effect of dissolved salts on the dissociation constant of water, but if, as recent experiments² seem to indicate the effect is to very slightly decrease the ionization, these figures represent the maximum correction. It is evident that as we approach pure water the conductivity not only becomes much smaller but has the additional advantage of becoming more constant. No water that has ever been used in the preparation of salt solutions

1. Kohlrausch and Heydweiller, Z. physik. Chem., 14, 317 (1894)

2. The influence of Electrolytes on the Dissociation Constant of Water. G. Poma and B. Tanzi, Z. physik. Chem., February, 1912. This work shows that the effect is small even in rather concentrated solutions of salts; in solutions so dilute as the ones in question it would, therefore, be negligible.

approaches the purity of the water referred to. That used by Kohlrausch and Malthy¹ had a conductivity twenty-five times as great.

Contamination of Solutions.

As to the contamination of solutions in the process of making or on standing for awhile in glass vessels one has only to observe the increase in the conductivity of fairly pure water when subjected to similar treatment. Water with a conductivity of $.25 \cdot 10^{-8}$ to $.3 \cdot 10^{-8}$ mhos in transferring from one vessel to another, unless special care is taken, will become contaminated sufficiently to increase the measurement to $.4$ or $.6 \cdot 10^{-8}$. Likewise an increase in conductance is observed in the course of a few minutes in water contained in the ordinary water conductivity cell. Kohlrausch and Maltby² concluded that even though exact measurements of .00001 N solutions were made, the change in conductivity due to pollution of the water was relatively so high that they could no longer attach any significance to the results. In this region they did not always find the equivalent conductance to be greatest at the highest dilution, e.g. at one, two and four, hundred-thousandth normal, the equivalent conductances of NaCl solutions were respectively, 108.86, 108.97 and 108.75. This problem, then is certainly an important one and the more important does it become the greater the dilution where the water correction is of most significance.

The Kohlrausch Method of Conductance Measurements.

Conductance measurements by means of the Wheatstone bridge with an induction coil as source of current and a telephone as balance indicator was described by F. Kohlrausch³ over thirty years ago. The method is the outgrowth of difficulties encountered in using a direct current and galvanometer due to polarization of the electrodes. Use of the alternating current to avoid polarization

1. Loc. cit.

2. Loc. cit.

3. Wiedemann Annalen, 11, 653 (1880)

had previously been made by Kohlrausch and Nippoldt¹ in 1869 and it is probable the telephone had been tried and discarded by others before Kohlrausch took it up in 1879 and made the application of it successful. Since that time the direct current and galvanometer have been but little used for electrolytic conduction measurements, their use being confined to exceedingly high resistances approaching a megohm in value. The bridge in the form used by Kohlrausch is shown in Fig. 1.

1. Pogg. Annalen, 138, 280 (1869).

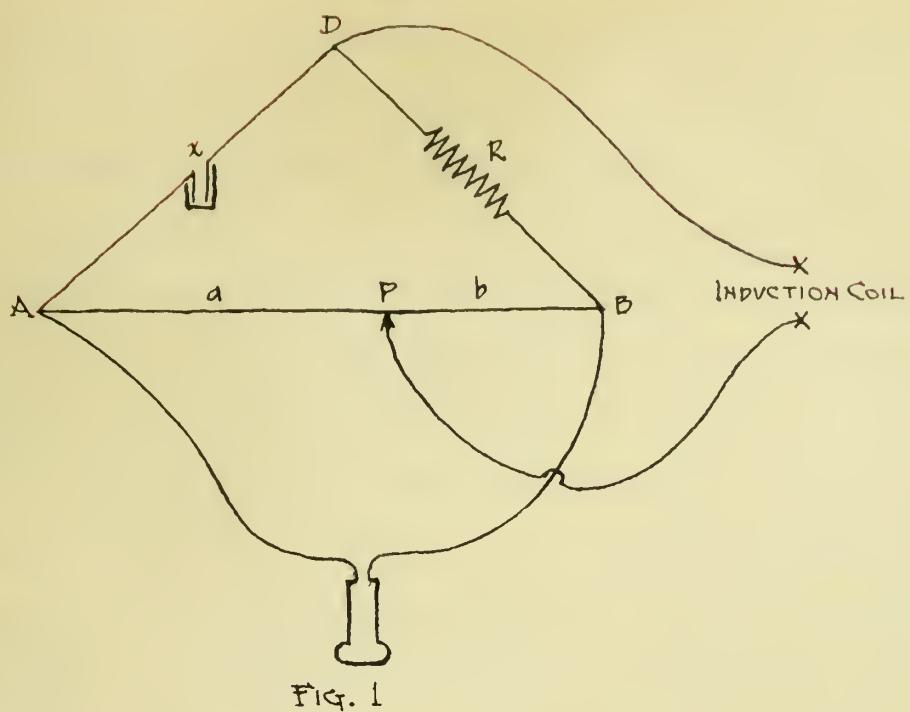


FIG. 1

Figure 1 shows the Wheatstone bridge in principle as modified by Kohlrausch for electrolytic resistances.

Many refinements have since been made in the apparatus so that much more accurate results are obtainable now than originally. Most of the improvements were made by Kohlrausch himself who increased the length of the bridge wire A B thus making it more sensitive to slight changes in the resistance x , and did various things to improve the minimum. The latter problem led him into an investigation¹ of the causes of and cures for poor minima, such as polarization, self induction capacity, etc., as well as the heating and consequent increase in conductivity of the electrolyte caused by the electric current. A brief discussion of some of these sources of error is given in the next few paragraphs.

Heat Effects.—The electrical energy dissipated in the form of heat when a current passes through a resistance is proportional to the length of time the current is passing, to the resistance and to the square of the current itself. If H is the heat generated, R the resistance, I the current and t the time, we may represent the relation by the equation

$$H = kRI^2t$$

where k is a constant depending on the units chosen for the variables H , R , I and t . The strength of current is, evidently, the factor with which we are most concerned, since it is the factor which when altered produces the greatest changes in the heat liberated. Now for a given potential difference between the electrodes, I varies inversely with R so that the product RI^2 , and consequently the rate of heating will increase as R is decreased and vice versa. That is heat troubles will be quite evident in good conductors and, other things being equal, of little consequence in very poor conductors, e. g., very dilute solutions.

To lessen this difficulty, which comes on especially in the measurement of more concentrated solutions, a small current is used. In practice this works out very nicely since, as will be seen later, polarization is thereby reduced,

1. Kohlrausch and Holborn, Leitvermögen der Elektrolyte.

also, and with even quite small currents a good minimum is easily obtained. The current can be decreased by increasing the distance between the electrodes thereby increasing the cell constant. If as is sometimes true there are still heat effects after all precautions are taken to obviate them, it will be evident from the "creeping" of the bridge reading toward the end of the wire adjacent to the cell. This can usually be reduced to a negligible quantity by exercising skill in obtaining the balance and thus keep the circuit closed for a brief time only. It is best under such circumstances to get the setting approximately and then break the circuit to let the solution come again to the constant temperature of the bath before taking the final reading. With practice the time necessary for making the final adjustment can usually be reduced to a very few seconds.

Polarization.-This phenomenon is a back E. M. F. and tends to decrease the effective potential difference impressed between the electrodes. It depends on the current density and the time during which the current flows in a given direction, i.e. for alternating currents on the current density and the frequency. For small current densities and short intervals of time it may be taken as directly proportional to each, i.e.

$$e = -k \int idt$$

It is negative since it acts in opposition to the impressed E. M. F.. Since e is proportional to the current density it is inversely proportional to the surface of the electrode so that platinized¹ electrodes or sand blasted ones tend to decrease polarization effects. Besides having additional surface platinized electrodes seem to absorb gases more readily and the sharp points of the platinum black seem to offer easy escape for bubbles of gas. "The platinum black

1. Kohlrausch has shown that well platinized electrodes may have several thousand times the surface of polished ones. Arrhenius Electrochemistry, p. 132 Eng. Ed.

acts as a medium to bring about equilibrium between the solutions of gases as formed in the cell and the gases in the space about the electrodes ¹."

In conductivity experiments polarization is most troublesome in the more concentrated solutions where the specific resistance is small and the currents are large. To obviate this difficulty the electrodes are usually platinized and placed rather far apart so as to decrease the current density. In this way one is able to obtain very good minima in moderately concentrated solutions but in the more concentrated ones polarization troubles again appear in spite of these precautions. Still another means of decreasing this evil remains, which has not hitherto been systematically applied, and that is by increasing the frequency of the alternating current. This fact has been taken advantage of in the use of the apparatus to be described here and very good minima have been obtained using quite concentrated solutions. In one case the ordinary dilute sulfuric acid of the laboratory - about six times normal - was used with very satisfactory results. With the ordinary induction coil used for conductivity measurements in which the frequency is low and adjustable only within narrow limits considerable difficulty would be met with in working with such solutions.

Self-Induction.—Self induction in a coil of wire is a function of the frequency, the current and the number of turns in the coil. It varies directly with the current, directly with the square of the number of turns and increases with increasing frequency. Resistance coils of standard makes are wound non-inductively which renders them nearly free from induction and it is questionable whether conductivity measurements suffer very much from this source of error. Kohlrausch says that only in the smaller resistances does it interfere since the larger ones cut down the current sufficiently to render induction negligible.

The bifilar winding, however, adds to the capacity effects and it is sometimes desirable to obviate this by using another system of winding. Since the induction varies with the square of the number of turns in a coil it rises very rapidly as the number of turns is increased so that if self induction is undesirable coils of few turns should be made. Induction in its effects is opposed to the effects of capacity so that they tend to neutralize each other. Furthermore a condenser can be used to counteract the effects of induction.

Capacity.-The most frequent and troublesome source of difficulty encountered in obtaining a minimum is that of capacity in the system. Whenever resistances above a few hundred ohms are to be measured capacity troubles set in and they increase as the resistances get larger. There are three different sources of capacity, viz.: the resistance coil of the ordinary standard boxes, the electrodes of the cell, and the cell itself. Ordinary resistance coils wound non-inductively by the bifilar method are a very fruitful source of capacity troubles. Not only do the turns of the coil itself act as condensers but the placing together of two wires, as in the bifilar winding, the terminals of which are in large resistances at quite a little difference of potential, makes the two wires act like the plates of a condenser. This is especially true of the very large resistance coils, capacity effects, unlike those of induction and polarization increasing with increasing resistances. Capacity effects also increase with the frequency, in this respect it is like inductance, and herein seems to lie the difficulty in neutralizing the composite effect produced when an induction coil of varying and various frequencies is used as a source of current.

The capacity of coils would be very much less if they were wound singly, i. e. according to the unifilar plan, but in that case we should have self-induction in place of the capacity. Some of the high grade resistance coils are wound, however, in such a manner as to do away with both self induction and ca-

1
pacity. The scheme used is that of the Chaperon¹ method, according to which it is claimed one can make resistance units of as great values as 100,000 ohms practically free from both of these evils. This is not true, however, of the ordinary high grade coils said to be wound according to the Chaperon principle, as they are not altogether free from these difficulties.

The capacity of the electrodes is usually not sufficient to cause any trouble² and would be only in cases where the cell constant is quite small, i. e. when the electrodes are very large and very close to each other. On the other hand difficulties sometimes arise due to charges on the walls of the cell³, especially if the latter is in a bath or only moist on the outside. Like other capacity troubles it is most serious when the cell is filled with a very poor electrolyte, i. e. when high resistances are concerned. It is remedied by using a non electrolyte, such as petroleum, as a bath liquid.

In spite of all precautions to eliminate capacity and induction there still remains one or the other to prevent good minima even in only moderately dilute solutions. To remedy this a condenser of variable capacity is put into the system parallel either with the cell or with the comparison resistance R. The location of the condenser depends on the location of the capacity in the system. It is placed where it will do the most good and the capacity is varied until that value is found which gives the best minimum⁴. The correct adjustment of the condenser is sometimes quite difficult to attain and can be obtained only after much changing of plugs and considerable expenditure of time. Still it is one of the most important factors in getting correct bridge settings and is absolutely

1. Chaperon, M. G., C. R., 108, 799 (1889).

2. Kohlrausch and Holborn, Leitvermögen der Elektrolyte, p. 58.

3. Kohlrausch and Holborn, ibid.

4. For this purpose Kohlrausch has devised a condenser containing units varying in value from 256, 128, 64, etc. down to $1/2$ so that it is possible to adjust the capacity to within $1/2$ of these small units. A more convenient type is described in this paper.

indispensable. In large resistances a very small change in capacity of the condenser will alter the quality of the minimum considerably. I have noticed, in determining the conductivity of water in which the temperature of the water had not yet acquired the temperature of the bath, and the bridge reading was, consequently slowly creeping, that the capacity with which a perfect minimum was obtained at one bridge reading was noticeably different from that with which a perfect minimum was obtained when the bridge reading had changed but a single space, the length of the bridge wire being 1000 spaces. This only shows how intimately related is a good minimum to the proper adjustment of the condenser and how important the latter instrument is in this kind of work. It also explains why poor minima are probably the rule in conductivity experiments rather than almost perfect ones.

From the foregoing discussion of sources of error and survey of the method in common use we get a fair conception of the problem of conductance measurements. We are also enabled to see why work has not been extended into the region of still more dilute solutions and why more reliance can not be placed upon some of the accepted values for the region that has been studied. It is clear that in any attempt to push the investigation into solutions of still lower concentrations, the mode of attack must contain a scheme for decreasing the water correction. Furthermore, this scheme must arrange both for getting purer water at the start and for preventing contamination in the process of solution making. These two factors are taken into account in the present work. The general plan consists in carrying out the entire procedure in vacuo, distilling the water directly into a vessel containing electrodes for measuring its conductivity and that of the solution. It likewise provides a means for introducing salts into the vessel without danger of admitting air. In this way errors due to contamination in solution making will be practically eliminated and those due to the

otherwise unavoidable water correction can by careful work be diminished to much smaller ones than is usually the case. In addition improvements have been made in the Kohlrausch apparatus so that the electrolytic resistances may be determined with a much greater degree of accuracy than has hitherto been done.

PART II

AN IMPROVED APPARATUS FOR MEASURING THE
CONDUCTIVITY OF ELECTROLYTES.

The problem demanded first of all a consideration of the Kohlrausch method in some of its details and its application to the measurement of electrical conductivities in aqueous solutions of strong electrolytes in the concentration range included between .001 and .000001 normal. As a result of a critical examination of the sources of error in this method when applied to solutions of such high specific resistances an apparatus has been evolved which permits the easy attainment of a very high degree of precision, not only in the measurement of very large electrolytic resistances but of very small ones as well. In addition to the increased degree of precision attainable with the improved apparatus, it possesses the advantage of greater rapidity and convenience, and the sharp, perfect minima, obtained relieve the nerves of the operator of the strain imposed by the effort to find the correct bridge setting with a poor minimum. The apparatus described below was designed to include all of the perfections of the most accurate apparatus employed by Kohlrausch¹ together with some additional improvements which permit the attainment of a degree of precision, about ten times that obtained by Kohlrausch in his most accurate investigations. This high degree of precision is, moreover, attained with the greatest ease and certainty as will be clear from the test experiments described below. A consideration of the theory of conductance measurements with the alternating current made it appear very probable that the precision of the method could be increased by making the following changes in the customary apparatus:

1. As described in the paper of Kohlrausch and Maltby, Abhandl. Physik. Tech. Reichsanstalt, 3, 157 (1900).

1. Abandon the induction coil as a source of current and replace it by a high frequency generator giving a pure current of a single frequency, one which is entirely free from the overtones which are present in the complex wave system obtained with the induction coil.

2. For measuring very high resistances (20,000 ohms or more) replace the ordinary resistance box by one in which the resistance units are free from both inductance and capacity.

3. Use a tuned telephone, and an "extended" bridge wire and make all measurements at the middle of the bridge. Take as much pains in balancing the capacities in the bridge arms as in balancing the resistances.

Description of the Apparatus.

The High Frequency Generator.-The only instrument on the market, as far as we were able to learn, which possessed most of the desired qualities was the "Small High-frequency Machine" manufactured by Siemens and Halske. This machine is shown in Fig. 2. It has a normal frequency of 1000 cycles per second but any desired frequency between 450 and 1800 cycles per second can be obtained by regulating the position of the eddy-current "brake" provided with the instrument. This instrument is mounted upon a felt pad in a room some distance from the conductivity laboratory and is inclosed in a box to protect it from dust and to shut in the sound emitted by the rapidly moving toothed wheel.

All of the connections for the instrument are brought to the main electrical distribution board of the building, so that the high frequency current may be sent to any room in the building. The starting rheostat and the eddy-current brake are placed in the conductivity laboratory, the latter instrument being mounted near the conductivity bridge, so that the operator can vary the frequency of his current at pleasure. The normal frequency of the instrument, 1000 cycles per second, is the best to employ in nearly all cases. Since, however,

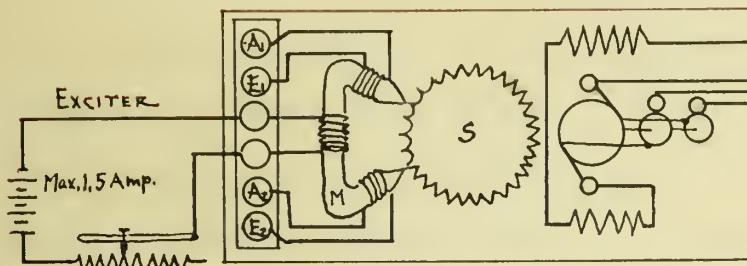


FIG. 2.

The toothed wheel S, when two teeth are adjacent to the poles of the electro magnet M, serves as a key, and a maximum number of lines of force passes. When the wheel has turned till each pole is midway between two teeth the lines of force are at a minimum. Thus, an alternating E. M. F. is set up between A₁ and E₁ and between A₂ and E₂. The frequency is varied by varying the speed of the wheel S. The current is taken from A₁, E₁ or A₂, E₂, or both.

the frequency depends upon the rate at which the motor is driven, it is influenced by any sudden change in the load on the 110 volt circuit from which the motor is operated. Such changes, if they are not too frequent, can be readily neutralized by shifting the position of the eddy-current brake, but if they are liable to occur frequently they become a source of considerable annoyance. It is best, therefore, to operate the machine on a circuit of constant potential. In most of the experiments described below the machine was driven from a small 110 volt generator which was protected from a varying load. Under these conditions it has never been found necessary to vary the frequency.

The current obtained from the high frequency generator is regulated by means of a rheostat mounted beside the starting rheostat of the generator, and connected in series with the exciting coil of the electro-magnet. The exciting current employed during the conductance measurements was varied according to the resistance of the cell, from 0.2 amp. for low resistances to 2.3 amp. for high resistances. The heating effect of the induced current in the cell, during the time required by the measurements, is scarcely appreciable with a properly designed cell, if an accuracy no greater than 0.01 per cent is sufficient.

The Special "Film" Resistance Units.—In order to prepare stable high resistances, practically free from either inductance or capacity, it is only necessary to seal two platinum wires into the ends of a glass rod and connect them by a thin film of platinum deposited upon the glass. For the preparation of thin metallic films of this character a number of different methods have been devised and published in recent years¹.

One of the most convenient methods makes use of a colloidal solution of the

1. L. Houllevigue, Compt. rend., 149, 1368; M. U. Schoop, Electrochem. Z., 17, 53; Met. Chem. Eng., 8, 404; H. G. Cannegieter, Z. biol. Technik. Meth., 2, 21; J. K. A. U., Salomonson, Z. biol. Tech. Meth., 1, 35-43; Leithäuser, Engineering, 86, 818.

metal in a suitable solvent. One of these solutions, under the name of "platinum-glanz," is extensively employed in making gas electrodes. In the later work a colloidal solution of chlorplatinic acid in oil of lavender was used. The chlor-platinic acid is triturated in an agate mortar with just enough of the oil of lavender to form a paste in which the acid particles are exceedingly small. To accomplish this the ingredients are added alternately in quite small amounts at a time followed always by much grinding with the pestle. When sufficient paste is made more oil is added, the mixture stirred and decanted after standing several hours to let the larger particles settle out. The procedure employed in making resistance units with this material is as follows:

Two lead wires of platinum are sealed into the ends of a U-shaped glass rod of suitable length. The joint between the glass and the platinum is then covered with a layer of the platinum-glanz and by means of a drawing pen a narrow line of the platinum-glanz is drawn along the surface of the rod so as to connect the two lead wires. After the layer of platinum-glanz is completely dry it is heated gradually to a dull red heat. This heating can, with care, be conducted in a flame, but it is safer to use an electric furnace. When the heating is completed the narrow line of platinum-glanz has been converted into a thin film of platinum which is fused into the glass so that it cannot be scratched with a knife. A resistance unit of 80,000 ohms can be obtained in this way upon a U-shaped, narrow, glass rod only 10 inches high.

When properly constructed and handled these resistances are very permanent. They have a temperature coefficient of 0.1 per cent per degree between 25° and 50°, and hence where an accuracy of 0.01 per cent is desired the temperature of the resistance box must be kept constant to 0.1° during the measurement. Our resistances of this type are mounted in regular resistance-box-form in an oil bath, provided with a thermometer, stirrer and heating coil. Since they are de-

signed to serve as secondary standards only, they are checked at frequent intervals against a standard resistance box, using a galvanometer and direct current.

The Telephone.-Two telephones connected by a head piece constitute the most convenient arrangement. Both telephones should be tuned to respond to the frequency of the current employed. Those employed in the experiments described below were constructed especially for this work and were tuned to a frequency of 1000. Such an instrument is extremely sensitive when employed in a circuit of its own frequency.

The Bridge.-When a precision of more than 0.05 per cent is desired in conductivity measurements it is necessary to lengthen the ordinary bridge wire. This is most conveniently accomplished by connecting to each end of the wire a resistance coil, having a resistance $4 \frac{1}{2}$ times that of the bridge wire itself.¹ The bridge employed in the experiments described below was the Leeds and Northup roller type, with two such coils mounted in the base so that by removing a couple of plugs the coils could be connected to the ends of the bridge wire. When these coils were so connected, the "extended" bridge wire thus obtained was equivalent to a wire 47 meters long. The smallest scale division was 3 mm. wide and corresponded to $1/20,000$ of the total length of the extended wire. Since the bridge setting could be easily read to less than 0.1 of a scale division, the error in a conductance measurement due to the error in reading the bridge setting could never amount to 0.2×0.0001 or 0.002 per cent, for a setting at the middle of the bridge.

The Condenser.-The type of condenser devised by Kohlrausch² and used chiefly in this sort of work is not well adapted for getting the best minima. This

1. Kohlrausch and Holborn, p. 43.

2. Loc. cit.

is especially true in cases such as I have mentioned, where the condenser adjustments for two resistances quite close together, are noticeably different. A better instrument is one whose capacity may be varied continuously from zero to the full capacity of the condenser. For the final adjustment, at any rate, an instrument of this kind should be available - one of the usual form being arranged in parallel with it if necessary. The condenser used in this work is made of two sets of semicircular brass plates with air as the dielectric. The plates of one set - consisting, of course, of alternate ones which are always charged alike - are fastened at the center of the circle to a shaft by means of which they can be rotated through 180° . Thus in one position of these plates they are altogether out of the immediate vicinity of the other set and the capacity of the condenser is zero. By rotating them the capacity is gradually increased until a maximum is reached when they are turned through 180° .¹

By using a condenser of this type it is quite easy to find the best adjustment when the bridge setting is in the vicinity of the correct reading. In turning the button of the condenser to the right or left one passes through a point of minimum sound just as in adjusting the bridge reading. By alternately adjusting the two instruments the best minimum is quickly and easily obtained.

The Commutator.-In order to eliminate contact resistances in all bridge connections a commutator is used, by means of which the cell and the comparison resistance may be interchanged. If readings are taken in both positions these errors may be entirely eliminated as well as any error in the sliding contact. If a_1 and a_2 are the readings of the bridge in positions (1) and (2) respectively and r the length of the bridge wire we get

$$X = R \frac{r + (a_1 - a_2)}{r - (a_1 - a_2)}$$

1. This instrument was devised and made in the department of physics and was loaned to me for this work.

where, as before, X is the electrolytic and R the comparison resistance.

The commutator is shown in Fig. 3. It consists of the mercury cups A, B, C and D in a block of paraffin about six inches square and three inches deep. The connection of A to B and C to D gives position (1) while A to D and B to C gives position (2). The additional mercury cup F is connected to the condenser and permits a quick change of the position of that instrument. When F is joined to B it is in parallel with the cell and when joined to D it is in parallel with the resistance R. Stout copper wires serve as connectors between mercury cups.

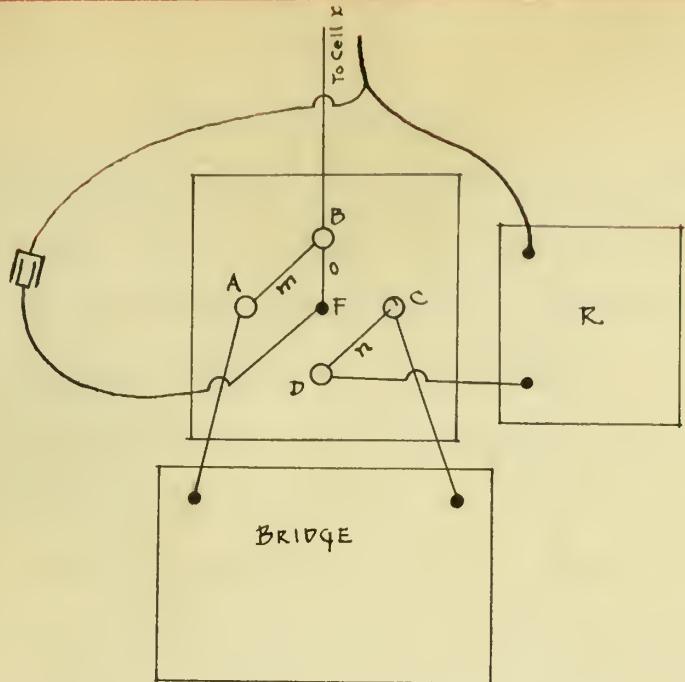


FIG. 3.

M and N are stout copper wires which serve simply to make connections between the mercury cups A, B, C and D. They are bent at right angles at each end so as to dip into two cups. o is a similar wire for joining F to B or D. R is the comparison resistance box showing only the terminals. The terminals of the slide wire bridge are shown at the lower part of the figure.

The Test Experiments.

In order to obtain definite figures illustrating the degree of precision attainable with the new apparatus a series of test experiments were carried out, in which, solutions of various concentrations were measured in different forms of cells. The cells employed in most of these experiments will be referred to as Nos. 1, 2, 3, and 4, respectively. They were of the pipet type described by MacInnes¹. The first three cells had platinized electrodes, 10 mm. in diameter and 75 mm., 15 mm., and 2 mm. apart, respectively. Cell 4 was fitted with two circular, unplatinized, platinum electrodes 30 mm. in diameter and 1.5 mm. apart. During the measurements the cells were submerged in a water thermostat maintained at room temperature to within 0.003° during the measurement of any cell.

The "extended" bridge wire was used in all the experiments and the high frequency machine was driven at its normal rate, giving a frequency of 1000 cycles per second. Except where otherwise specified the resistance boxes employed were standard, high grade boxes with manganin resistance coils. The special "film" resistance box described above was employed only in the measurement of very high resistances.

In order to eliminate the personal element as far as possible most of the measurements were made in triplicate, that is, the bridge setting for each cell was determined independently by three different observers². In recording the results thus obtained, the value for the resistance of the cell (in ohms) obtained by each observer is given, together with a statement of the number of scale divisions through which it was necessary to swing the contact in deciding the proper setting. A "perfect minimum" means that perfect silence was obtained at one point and that a sound was heard if the contact was moved more than 0.1

1. Dissertation 1911; J. Am. Chem. Soc., 33, 1688 (1911).

2. I wish to acknowledge my obligations to Mr. G. Y. Williams for his efficient assistance in carrying out this series of test experiments.

scale division on either side of this point. In this connection it may be noted that the tones obtained on the two sides of the minimum were identical in all their properties and were perfectly clear and of uniform quality.

As a basis for comparison of the degrees of precision attained in the different experiments the mean of the three results is given, together with the maximum and the average deviations from this mean, expressed in per cent.

Experiment 1.-The electrolyte was 0.1 N KCl and its resistance in cell No. 1 was determined. The results in ohms obtained by the three observers are as follows: 248.177, 248.172, 248.182; mean, 248.177; max. d., 0.002 per cent; a. d., 0.0014 per cent. Perfect minimum.

Experiment 2.-0.01 N KCl in cell 2. Resistance, 414.854, 414.862, 414.867; mean, 414.861; max. d., 0.0017 per cent; a. d., 0.0012 per cent. Perfect minimum.

Experiment 3.-0.001 N KCl in cell 2. Resistance, 4007.60, 4007.60, 4007.76; mean, 4007.65; max. d., 0.0027 per cent; a. d., 0.0017 per cent. Perfect minimum.

Experiment 4.-0.001 N KCl in cell 3. Resistance, 541.779, 541.774, 541.794; mean, 541.782; max. d., 0.0018 per cent; a. d., 0.0015 per cent. Perfect minimum. Owing to the small heat capacity of the thin film of liquid between the electrodes in this cell, the heating effect of the current made it necessary to make the final bridge setting very quickly. The time consumed in this operation varied from 6.4 sec. to 8.0 sec. with the different observers.

Experiment 5.-0.0001 KCl solution in cell 2. Resistance, 30,892, 30,894; mean, 30,893; dev., 0.003 per cent. Minimum extended through 3 scale divisions.

Experiment 6.-Identical with experiment 5 except that the special "film" resistance box was substituted in place of the Hartman and Braun box used in experiment 5. Resistance, 28,895.8, 28,896.3; mean, 28,896.0; dev., 0.0011 per

cent. Perfect minimum. A comparison of the results of experiments 5 and 6 shows the improvement in the minimum effected by use of the film resistances.¹

Experiment 7.-Conductivity water having a specific conductance of $0.9 \cdot 10^{-6}$ mhos at the temperature of the experiment was measured in cell 4. Resistance, 33,185, 33,191; mean, 33,188; dev., 0.012 per cent. Poor minimum. No point of complete silence could be found. A swing of 12 scale divisions was necessary in estimating the bridge setting.

Experiment 8.-The same as experiment 7 except that the special "film" resistance box was employed. Resistance, 32,857.9, 32,857.9, 32,857.9; mean, 32,857.9; dev., 0.0 per cent. Minimum good, perfect silence being obtained. Range of swing 4 scale divisions, with sharp appearance of the sound at each end of the swing. The advantage of the "film" resistances is again evident from the results of experiments 7 and 8. The next three experiments deal with solutions of high specific conductance.

Experiment 9.-Normal KBr in cell 1. Resistance, 27.9293, 27.9296, 27.9296, mean, 27.9295; max. d., 0.0007 per cent; a. d., 0.0005 per cent. Perfect minimum. This experiment shows that polarization has no influence upon the minimum at this concentration.

Experiment 10.-6 N H₂SO₄ in an Arrhenius cell with the electrodes 10.2 cm. apart. Resistance, 1.5506, 1.5512, 1.5518; mean, 1.5512; max. d., 0.04 per cent a. d., 0.028 per cent. Minimum very poor. Length of swing 40 scale divisions. The disturbing effect of polarization is evident in this experiment. It can be largely eliminated, however, by employing a properly designed cell, as is evident from the results of the next experiment.

1. The difference in the absolute values of the resistances given in experiments 5 and 6 is not significant, as the values used for the resistance units of the "film" resistance box are only approximate. No attempt was made to standardize these resistances for this set of experiments.

Experiment 11.-6 N H₂SO₄ in a special high resistance cell (Kohlrausch and Holborn, fig. 10, p. 16) fitted with platinized electrodes 3 cm. in diameter. Resistance, 149.401, 149.407, 149.425, 149.407; mean, 149.410; max. d., 0.010 per cent; a. d., 0.005 per cent. Minimum fair. Range of swing, 1 scale division. Complete silence was not obtained.

Experiment 12.-In measuring the resistance of very dilute solutions, fair results can also be obtained with a small induction coil, provided that "film" resistances are employed instead of the standard type of resistance box. The following results were obtained in this manner for a 0.0001 N KCl solution in cell 2. Resistance, 28,927.6, 28,928.9; mean, 28,928.2; dev., 0.003 per cent. Minimum good. Perfect silence was obtained. Range of swing 3 scale divisions (cf. Exp. 6).

When the standard resistance box was used the following results were obtained. Resistance, 30,096, 30,102; mean, 30,099; dev., 0.01 per cent. Minimum very poor. Silence could not be secured at any point. Range of swing, 20 scale divisions (cf. Exp. 5).

Discussion of the Experiments.

The results obtained in the test experiments indicate very clearly that with the improved apparatus the conductivity of any solution of an electrolyte from conductivity water itself up to a several-times-normal solution can be determined with a precision of 0.01 per cent with the greatest of ease, and that by careful work this degree of precision can be raised to 0.001 per cent in most cases.

Although a precision of a few thousandths of 1 per cent can be obtained with this apparatus, the attainment of an equal degree of accuracy is of course quite another story, involving as it does the elimination of all sources of constant error, amounting to 0.001 per cent or more.

In cases where changes in conductance, only, are involved, however, constant sources of error are not necessarily objectionable. An example of this occurs in transference measurements by the Hittorf method. At the completion of such a transference experiment it is first necessary to discover whether the concentrations of the three middle portions are identical or not. This can be very quickly and accurately determined by finding successively the bridge settings for each solution in the same conductance cell. This method will usually result in the saving of a considerable amount of time, since in exact work these concentrations must be determined with an accuracy of at least 0.01 per cent. The new apparatus should prove of considerable value in all cases where a very exact analytical control of pure solutions of electrolytes is desired.

PART III

PREPARATION AND PRESERVATION OF SOLUTIONS.

Preparation of Pure Water.—Attention has already been called to the necessity of having water of low conductivity for the preparation of solutions. It has also been pointed out that the best water hitherto used for conductance work was that made by Kohlrausch and Maltby¹ with a specific conductivity of $.9 \cdot 10^{-6}$ mhos at 18° C , which when used for preparation of NaCl solutions at .0001 normal involved a water correction of about 10 per cent. Now, it is a comparatively easy matter to get water much purer than this from a good still made of copper and lined throughout with block tin. There is a still of this description in this laboratory which has a capacity of about 50 liters and from which good water is obtainable. By carrying out the distillation in air water has been obtained with a specific conductance about five times smaller than the water used by Kohlrausch and Maltby.

In order to get the best water the still is filled with the ordinary distilled water of the laboratory to which are added 150 cc. of an alkaline permanganate solution containing 8 g KMnO₄ to 200 g KOH in a liter of solution. The contents of the still are then heated by a steam heating coil until water begins to come over, when the steam is turned off. It is allowed to stand over night and the distillation carried out the next day. The first part of the distillate - eight to ten liters - will contain practically all of the ammonia and is rejected; good water can now be collected. The end of the block-tin condenser tube is extended into the mouth of the collecting bottle and the water collected in an atmosphere of steam. For the best results it is necessary to have the steam only partially condensed to liquid water and, consequently

1. Loc. cit.

a vigorous current of steam constantly issuing from the mouth of the bottle. The water thus collected is boiling hot. If these precautions are observed, it is a simple matter to get water which has a specific conductance of $.25 \cdot 10^{-8}$ reciprocal ohms at 25° C . Water of this purity has repeatedly been obtained by both Mr. Williams and myself. By taking special precautions, such as, repeatedly rinsing the collecting bottle with the boiling hot distillate, collecting in an especially vigorous current of steam and taking the distillate after the still was half emptied, water has been found with a specific conductance of $.19 \cdot 10^{-8}$ reciprocal ohms at 25° C . This sample for water conductivity cell was taken from the bottle filled up nearly to the top of the ground glass part and while the distillation was still going on. The conductivity arose, on standing sixteen hours in the collecting bottle, to $.27 \cdot 10^{-8}$. So far as I have been able to learn this is the purest water that has been obtained by distillation in air. A second attempt gave water with a specific conductance of $.22 \cdot 10^{-8}$ mhos. It was evident, however, that the conditions were not so favorable as in the previous case.

It does not seem probable that water of much greater purity than this can be obtained by a single distillation in air. It might be improved considerably by a second distillation, especially, if some phosphoric acid were added to the second still in order to liberate any carbon dioxide, which could be collected in the first distillate and rejected. With this end in view a second still similar to the first was built. Its capacity, however, is only 30 liters and it was made higher than the first one with a block tin condenser tube running more than a meter above the still itself and measuring in all over three meters in length. This still connects directly with the long condenser tube of the first still.

When the impurities always present in a new still are completely washed

out, it is expected that a double distillation will materially improve on the quality of our best water. At present the new still is not free from impurities, but they are rapidly being removed as is shown by the fact that each distillation gives better water than the previous one.

Preservation of Water.-Exposure of very pure water to contact with ordinary air, if only for a few minutes, suffices to materially increase the conductivity. Protecting it from the atmosphere, however, shows that the conductivity is much more constant. This constancy depends on the efficiency of the protection. If ground glass stoppers are used they may furnish ample protection after they are inserted, but in putting them in place or removing them small particles of impurities that have collected about the mouth of the vessel may be loosened and fall in. Furthermore, by turning the stopper and rubbing together the ground surfaces, very small particles of glass may be formed which have a greater polluting power than other glass. (It seems probable that water in contact with a ground glass surface is more easily contaminated than if in contact with glazed surfaces only.)

A better means of protection is to cover the bottle (or flask) with a watch glass and invert over it a beaker, just large enough to slip over the neck of the bottle. A still better way is to cover with several layers of tin foil, pressing it down around the mouth of the bottle to render the passage of air difficult. The tin foil should be thoroughly steamed before using. Both of these schemes employ the better plan of having a covering fit over the mouth of the bottle rather than something to fit into it. Using tin foil, Williams, who suggested it, kept water for a day before its conductivity rose to $.36 \cdot 10^{-6}$ and for several weeks before it rose to $.6 \cdot 10^{-6}$. Recently, I have kept the best water yet obtained for sixteen hours in a resistance glass bottle with the conductivity rising only from $.19 \cdot 10^{-6}$ to $.27 \cdot 10^{-6}$ at 25°C . This water

was boiling hot at the beginning and was in contact with ground glass until on cooling contraction brought it down out of the ground glass mouth of the bottle.

The only perfect way of preventing contamination by the air is to distill in vacuo and collect in an air tight vessel. If this vessel is made of the best glass, such as Jena - gordite or resistance glass the contamination will be very little indeed. In this case as in all others it is essential to wash and steam the vessel repeatedly in order to remove all traces of dirt or soluble parts of the glass. After many trials I was able to keep water that measured $.21 \cdot 10^{-8}$ mhos at 0° for twelve hours without any appreciable change in its conductivity. This is ample time for making up solutions and measuring their conductance. With water of this purity, if the work is done in vacuo, reliable results should be obtained from .0001 N solutions, and from .00001 N solutions results should be as reliable as the present figures on .0001 N solutions.

Biographical.

The writer received his early education in the public schools of Ohio and his college preparatory work in the school now known as Ohio Northern University. In 1903 he went to The University of Chicago where after two and a half years' work he received the S. B. degree in 1905. During the years 1905-08 he was teacher of chemistry and physics in Ottawa, Illinois, Township High School. In 1908 he returned to The University of Chicago for two years of graduate work and in 1910 went to The University of Washington for one year as instructor in chemistry. From 1911 to 1913 he has done graduate work and teaching in the department of chemistry of The University of Illinois.





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